Solid State Ionics 16 (1985) 67-72
North-Holland Publishing Company

TETRAGONAL ZIRCONIA: WET CHEMICAL PREPARATION, MECHANICAL AND ELECTRICAL PROPERTIES

K. KEIZER, M. VAN HEMERT, M.A.C.G. VAN DE GRAAF and A.J. BURGGRAAF

Twente University of Technology, Department of Chemical Engineering, Laboratory of Inorganic Chemistry, Materials Science and Catalysis, P.O. Box 217, 7500 AE Enschede, The Netherlands

Yttria-stabilized zirconia powders were prepared in the composition range of 3 to 13 at% yttria. The hydrolysis-gel precipitation technique was used, starting from metal alkoxides or chlorides. In the composition range between 5 and 10 at% yttria, the materials sintered at 1250°C have a fully tetragonal structure. The density was higher than 95% and the grain sizes can be varied between 0.1 and 0.5μm depending on the preparation conditions. The fracture toughness K_{IC} amounts 6 to 11 $MPam^{\frac{1}{2}}$ but is not dependent on the composition. The transformation toughening mechanism and the properties of the tetragonal phase itself play an important role in the increase of K_{IC} compared with cubic materials. The magnitude of the oxygen-ion conductivity value is comparable with that for cubic materials.

1. INTRODUCTION

Zirconium oxide has a monoclinic(M) structure at room temperature. According to the phase diagram of Scott[1] in the system ZrO_2-Y_2O_3 the cubic (C), fluorite phase is stabilized at room temperature at an yttria concentration of 17 at.%. Between these two single phase regions several two-phase mixtures exist. These phase mixtures consist of M+C at room temperature and M+T or T+C at higher temperatures (T=tetragonal phase). However, at temperatures between 800K and 1400K a monophasic tetragonal phase region exists between $YO_{1.5}$-concentrations of 0 and 5 at.%. In 1965 Garvie[2] succeeded in preparing the tetragonal phase at room temperature. Garvie et al.[3] reported that a dispersion of this metastable tetragonal zirconia in grains of cubic stabilized zirconia ceramics resulted in a relatively tough material. Introduction of small tetragonal zirconia particles in, for instance, alumina enhanced also the fracture toughness[6]. The mechanism of stress-induced phase transformation was introduced to explain the increase of fracture toughness and strength of the partially-stabilized as well as tetragonal materials[3,4,5] and composite materials. The mechanism suggests, that a transition from the tetragonal to the monoclinic phase in front of a crack is capable of absorbing energy that would otherwise be available for crack extension. Another reason for energy absorption can be the volume change that occurs during phase transformation. The stress-induced transformation is then accompanied by the formation of a small crack in the vicinity of the transformed particle. The formation of many small cracks in front of a larger crack would greatly increase the amount of surface area formed per unit extension of the larger crack and thus increase the energy absorbed during crack extension. To obtain a tetragonal phase at room temperature grain sizes between 0.2 and 1.0μm depending on the yttria content[19] are necessary in the ceramic material, but according to Garvie and Gupta[4,5] grain sizes less than 0.4μm are used. However, small grain sizes in fully cubic zirconia materials increase the fracture toughness and strength too[7]. Michel et al.[8] and Ingel et al.[9,10] prepared single crystals in the ZrO_2-Y_2O_3 system with 4 to 6 wt% yttria by skull melting. Using a rapid cooling process (400°C/hr) these materials were 100% tetragonal and no monoclinic phase could be detected in fracture surfaces. These single crystals have a domain structure, because of the

0 167-2738/85/$ 03.30

cubic to tetragonal transition at 2000°C. This is one of the reasons that the tetragonal phase is stabilized at room temperature. The large strength and toughness relative to cubic materials was maintained above the monoclinic-tetragonal transformation temperature. These results demonstrate that besides transformation toughening other effects are important with respect to increasing strength and toughness. These effects are the grain size and the presence of the tetragonal phase itself, because the fracture in tetragonal material occurred along other crystallographic planes than in cubic material.

In this paper polycrystalline tetragonal materials are presented. Both mechanical and electrical properties are measured and discussed in comparison with literature data on partially-stabilized(PSZ), tetragonal and fully-stabilized zirconia. Special attention was given to the effects of powder preparation and sintering procedure and on grain boundaries.

2. EXPERIMENTAL

Yttria-stabilized zirconia powders $Zr_{1-x}Y_xO_{2-\frac{1}{2}x}$ in the composition range $0.03<x<0.13$ were synthesized by hydrolysis-gel precipitation starting from metal alkoxides or chlorides, as previously described[11,12] and calcined at 550°C. Ceramic samples were prepared by isostatic compaction at 400 MPa and subsequent sintering in air. All samples were prefired at 900°C and further sintered at temperatures up to 1200°C in one or more steps (Table I). X-ray fluorescence spectroscopy was applied for the analysis of the overall composition[13]. Specific surface areas of the powders were determined according to the BET-method using the equipment described by Bosch et al.[14]. Ceramic densities were measured using the Archimedes method. Phase analyses were carried out by means of X-ray diffraction, using a Philips X-ray diffractometer PW 1710 with CuKα-radiation. A Jeol-JSM 35CF scanning electron microscope was used for the observation of grain sizes on polished and thermally etched samples.

TABLE I
The structural parameters of zirconia-yttria samples sintered at 1250°C in a single step.

Sample[1] code	S_{BET} (m^2/g)	dens. (%)	average grain size (μm)	X-ray diffraction phases[2]	c/a-ratio
C3.3	86(4)*	97	0.42(4)*	T+M	-
A5.3	109(4)	97	0.41(2)	T	1.015
A7.3	117(2)	98	0.39(2)	T	1.013
C5.6	96(3)	96	0.25(4)	T	1.016
C7.8	-	95	0.29(4)	T	1.012
C6.5	98(3)	97	0.31(3)	T	1.014
C8.9	113(2)	96	0.29(2)	T	1.011
C10.6	-	94	0.26(2)	T(or C)	1.000?
C12.8	-	94	1.04(5)	C	1.000

1. A = alkoxide synthesis; C = chloride synthesis. The number is the yttria content in at.%
2. T = tetragonal phase; M = monoclinic phase; C = cubic phase.

* Standard deviation in the last figure is given in parentheses.

Fracture toughness K_{IC} and strength σ_f were measured by means of a three-point bending test at a cross-head speed of $5\mu m.sec^{-1}$ with samples of 1x3x15 mm. The notch width was $50\pm5\mu m$ and no precracking was applied.

A Solartron 1174 frequency response analyser was used for a.c. conductivity measurements on disc-shaped samples with sputtered platinum electrodes. These measurements were carried out in the temperature range from 550 to 925K.

3. RESULTS AND DISCUSSION

3.1. Ceramic sample characterization.

In Table I characteristics of zirconia-yttria powders and ceramics are shown. The BET-surfaces of the powders are of the order of 100 m^2/g and there is not much difference between the alkoxide and chloride syntheses. The densities are between

94 and 98% for this single step procedure. In multistep sintering procedures higher densities can be obtained (99+%) even at lower temperatures and with grain sizes of about 0.1μm. A further discussion of these results will be published elsewhere[20]. The grain sizes mentioned in this table are 0.3 to 0.4μm after correction according to Mendelson[15] but in a cubic material the grain size is 3 times larger and the grain size distribution is broader. In most cases grain size is the smallest in chloride materials. Materials with a composition between 5 and 10 at% yttria are fully tetragonal as determined with X-ray diffraction. No monoclinic or cubic phase could be observed. In this region a monophasic solid solution appears with a decreasing c/a-ratio with increasing yttria-content. This is in agreement with Vegard's rule. Introduction of 5% (chloride material) to 20%(alkoxide material) monoclinic phase was possible by thoroughly grinding of the material. It should be noted, that the X-rays have a certain penetration depth of 20-40μm under the measuring conditions used and therefore the amount of monoclinic phase mentioned may be slightly dependent on measuring conditions. In the sample with 10.6 at% yttria the grain growth kinetics proceed as in a tetragonal material but the tetragonal distortion was very difficult to determine.

So fully tetragonal materials were found and in most cases no PSZ materials.

3.2. Mechanical properties

The fracture toughness K_{IC} and some values of the flexural strength are given in Table II. The fracture toughness values vary between 6 and 11 $MPam^{\frac{1}{2}}$, but there is no systematic relation with the yttria content. It should be noted, that the mixed (T+M)-sample C3.3 has a very high K_{IC}-value. For the cubic samples the fracture toughness is smaller, especially for the sample C12.8. With the results given in Table II again no suggestion can be given whether the sample C10.6 is cubic or not. The flexural strength values are of the order of 500 MPa and are somewhat lower than those given by Gupta[4,5].

TABLE II
The fracture toughness and flexural strength of the samples mentioned in table I.

Sample code	Fracture toughness ($MPa.m^{\frac{1}{2}}$)	Flexural strength (MPa)
C3.3	10.8(1)*	-
A5.3	6.3(5)	480(120)
A7.3	7.2(9)	-
C5.6	6.5(8)	-
C6.5	10.0(9)	-
C7.8	7.1(7)	550(80)
C8.9	8.1(6)	-
C10.6	5.4(6)	-
C12.8	3.3(4)	-

* Standard deviation in the last figure is given in parenthesis

Furthermore these results support the X-ray diffraction results, which only indicate the presence of the tetragonal phase in the composition region between 5 and 10 at% yttria.

3.3 Electrical properties

The bulk and grain boundary resistivity were determined separately with the frequency dispersion method for several samples. In fig.1 an example is given of a typical Arrhenius plot of the resistivity of bulk and grain boundary of the samples ZY C6.5 and ZY17[16] as a function of the temperature. The activation energies (E_a) of bulk and grain boundary resistance are determined using the equation:

$$T/\rho = 1/\rho_o.\exp(-E_a/RT) \quad (1)$$

where ρ is the specific resistance.
The calculated data are shown in Table III. In the composition range 5.3 to 8.9 at% yttria there is almost no difference in bulk resistance

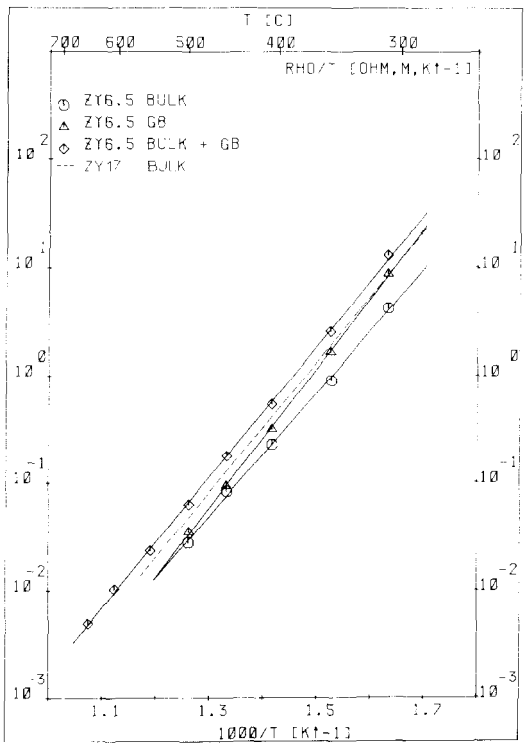

FIGURE 1

The bulk and grain boundary resistance of ZY6.5 (C6.5) and cubic ZY17 as a function of the temperature.

TABLE III

The activation energy and preexponential factor (ρ_0) values of grain boundary and bulk resistivity of several samples given in table I.

Sample code	log ρ_0(b) (ΩmK^{-1})	E_a(b) (kJ/mol)	log ρ_0(gb) (ΩmK^{-1})	E_a(gb) (kJ/mol)
A5.3	-8.52(6)*	102(1)	-9.38(9)	116(1)
C6.5	-8.10(17)	97(2)	-8.89(11)	109(1)
A7.3	-8.01(17)	95(1)	-8.89(12)	109(1)
C8.9	-8.25(15)	98(2)	-8.81(13)	108(2)
C12.8	-8.93(30)	104(4)	-8.84(11)	112(1)

* The standard deviation in the last figure is given in parentheses

and this bulk resistance is about the same as reported for cubic material (ZY 17, Verkerk[16], see Fig. 1). For the grain boundary resistance the grain size is an important faktor, i.e. the total grain boundary resistance is larger with smaller grain sizes. Therefore the specific resistance per grain boundary ($\rho_{gb}*d_g$; d_g= grain size)[17] is shown as a function of temperature in Fig.2. For comparison the grain boundary resistance of two commercial tetragonal materials (curve 5 and 6) presented by Bonanos et al.[18] (composition 5.5 at% yttria) are shown.

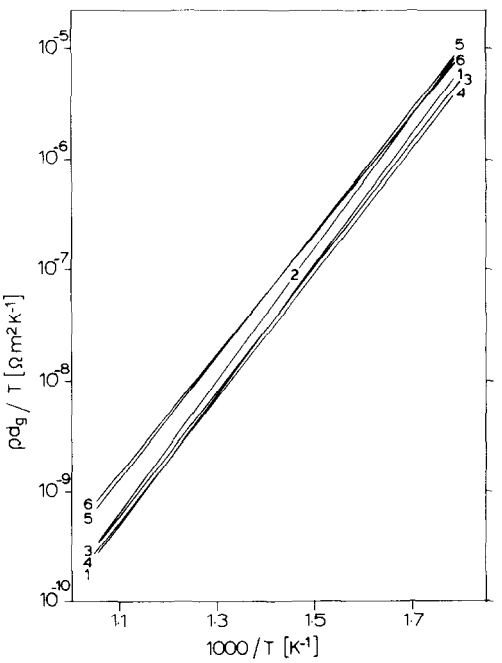

FIGURE 2

The specific resistance per grain boundary ($\rho_{gb}*d_g$) as a function of temperature for several samples (1=ZY17, grain size 1.11μm; 2=A5.3; 3=C6.5; 4=C7.8 and 5 and 6 are two commercial samples mentioned by Bonanos et al.[18]. The sample code is given in Table 1.

Although these resistances are somewhat higher than in our samples, due to a larger amount of impurities, the difference is not very large.

The bulk resistance values of these commercial materials are about the same as those given in Fig.1.

From these results it can be concluded that the occurrence and the degree of tetragonal distortion has almost no effect on the electrical behaviour and because of the lower yttria concentration and better mechanical properties than cubic material, this tetragonal material is preferred to cubic material for electrical applications. However, it is necessary, that no change in properties occurs during the application at temperatures of 500 to 800°C.

3.4 Discussion

In the introduction a survey is given on phases in the system zirconia-yttria and the toughening of the tetragonal phase. From our results and in our opinion tetragonal materials are not only stabilized at 5 at% (3 mol%) yttria but there is a whole composition range between 5 and 10 at% yttria where a fully tetragonal phase can be stabilized provided the grain size does not exceed a certain maximum value. In this region the sintering behaviour, the electrical and mechanical properties do not change much. This maximum value can be dependent on the composition because the tetragonal distortion is also a function of the composition. Samples with very small grain sizes can be prepared with a multistep sintering procedure. Outside the tetragonal composition region the sintering behaviour and the mechanical properties are different. The K_{IC}-value of sample C12.8 (cubic structure) fits in the relation for the fracture energy as a function of the grain size given by Winnubst et al.[7]. This may imply, that also such a relation exists for the tetragonal phase down to grain sizes of 0.3μm. In that case toughening of the tetragonal material may be caused by grain size effects as well as by the presence of a tetragonal material. Results concerning grain size effects at very small grain sizes will be published elsewhere[20]. The transformation toughening mechanism is then one of the three possibilities to increase the fracture toughening value.

4. CONCLUSIONS

Tetragonal zirconia is prepared in the system zirconia-yttria for compositions between 5 and 10 at% yttria. Densities larger than 95% and grain sizes smaller than 0.4μm can be achieved at temperatures of 1250°C. The powder synthesis method and sintering procedure can have large effects on the grain size at 95^{+}% densities. The mechanical properties are independent of the composition in this region and have the same values as are mentioned for tetragonal material in literature. The ionic conductivity of tetragonal materials is about the same as for cubic materials (at the composition with the highest conductivity (17 at% yttria)). The presence of the tetragonal phase itself is, besides transformation toughening, responsible for the toughening.

ACKNOWLEDGEMENTS

We would like to thank Koji Ioku of Sophia University, Tokyo for performing some experiments in our laboratory, Mr. J. Boeysma for X-ray diffraction experiments, Mr. de Jongh for SEM measurements and Dr. Winnubst for the stimulating discussions and mechanical measurements.

REFERENCES

1. H.G. Scott, J.Mater.Sci. 10 (1975) 1527
2. R.C. Garvie, J.Phys.Chem. 69 (1965) 1238
3. R.C. Garvie, R.H.J. Hannink and R.T. Pascoe, Nature 258 (1975) 703
4. T.K. Gupta in Fracture Mechanics of Ceramics, Vol.4 eds. R.C. Bradt and D.P.H. Hasselman (Plenum Publishing Corporation, 1978) 877
5. T.K. Gupta, F.F. Lange and J.H. Bechtold, J.Mater.Sci. 13 (1978) 1464

6. N. Claussen, J. Steeb and R.F. Pabst, Cer. Soc.Bull. 56 (1977) 559

7. A.J.A. Winnubst, K. Keizer and A.J. Burggraaf, J.Mater.Sci.18 (1983) 1958

8. D. Michel, L. Mazerolles and M. Perez y Jorba, J.Mater.Sci. 18 (1983) 2618

9. R.P. Ingel, R.W. Rice and D. Lewis, Comm.Amer. Ceram.Soc.July (1982) C-108

10. R.P. Ingel. D. Lewis, B.A. Bender and R.W. Rice, Comm.Amer.Ceram.Soc. Sept. (1982) C-150

11. M.A.C.G. van de Graaf, J.H.H. ter Maat and A.J. Burggraaf, in Ceramic Powders, ed. P. Vincenzini (Elsevier Publishing Company, Amsterdam, 1983) 783

12. M.A.C.G. van de Graaf, accepted for publication in Advances in Ceramics, vol.12

13. H. Kruidhof, Anal.Chim.Acta 102 (1978) 177

14. H. Bosch and A. Peppelenbos, J.Phys.E: Sci. Instrum. 10 (1977) 605

15. M.I. Mendelson, J.Amer.Ceram.Soc. 52 (1969) 443

16. M.J. Verkerk, thesis, T.H. Twente (1981)

17. M. Miyayama and H. Yanagida, Comm.Amer.Ceram. Soc. Oct. (1984) C194

18. N. Bonanos, R.K. Slotwinski, B.C.H. Steele and E.P. Butler, J.Mater Sci. Lett.3 (1984) 245

19. F.F. Lange, Proc.3rd.Int.Conf.Mech.Beh.Mater., Vol.3 (Pergamon, Oxford, 1980) pp. 45-56

20. M.A.C.G. van de Graaf, A.J.A. Winnubst, K. Keizer and A.J. Burggraaf, to be published in Science of Ceramics 13 (1985).